REPORT 25,151

FEASIBILITY STUDY OF OXYGEN/HYDROGEN POWDERED METAL IGNITION

First Quarterly Progress Report

16 September to 15 December 1964

21 December 1964

ASTRO

The Marquardt Corporation
Van Nuys, California

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I.   SCOPE OF WORK

The technical goals of the program are indicated below for clarification, and are as follows:

1. Analytically investigate the feasibility of using metal powders as catalysts for hypergolic ignition of hydrogen-liquid oxygen mixtures.

2. Select the metal powders which appear most promising theoretically, then experimentally determine the ignition characteristics of hydrogen-liquid oxygen combustion ignited through the use of each type of powder. The parameters will be varied according to the following:

   a. Hydrogen temperature, 40°R to 140°R

   b. Combustion chamber pressure, 0.5 psia to 15 psia

   c. O/F ratios, 4.0 to 6.0 and 0.5 to 1.5

   d. Powder concentration will be varied as required to achieve satisfactory ignition.

3. Investigate the effect of variables which might be a problem in actual rocket engine systems using powdered metal ignition. A list of these variables will include, but will not be restricted to:

   a. Partial oxidation of the powder

   b. Powder particle agglomeration

   c. Powder particle size.

4. Consider the relative merits of:

   a. Mixing powder with liquid hydrogen in the propellant tank, and

   b. Injecting powder into the combustion chamber or hydrogen feed line;

   and also consider the effects of metal powders on turbine bearings, valves, etc.

II.   PROGRAM PLANNING

For planning purposes, the research program has been divided into the following phases:

Phase I.   - Analytical Studies

Phase II. - Planning of Experimental Program

Phase III. - Experimental Study

Phase IV. - Evaluation of Experimental Data

It is intended that Phase I - Analytical Studies include a review of the chemical literature on catalysts and pyrophoric metals which could be useful as potential ignition components in the study. This phase also includes evaluation of a basic theory of catalytic ignition, on the basis of which an important portion of the experimental program will be undertaken. Phase II - Planning of Experimental Program includes the engineering analysis and design of a quantitative experimental apparatus, together with the development of a proposed technique for experimentally evaluating potential ignitors. Much of the Phase II study has been completed and procurement of equipment has been started. Phase III - Experimental Study represents the major experimental program effort which will be conducted in a laboratory-scale type of apparatus. A preliminary laboratory screening of some potential catalysts has been successfully initiated. Phase IV - Evaluation of Experimental Data represents the detailed review and analysis of the experimental data which will be obtained in Phase III.
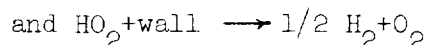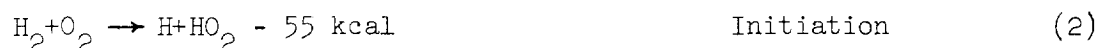
III.   CURRENT PROGRESS

Phase I - Analytical Studies

1.   Analysis of Experimental Models

The basic technical problem is to produce the ignition of mixtures of hydrogen and oxygen at O/F ratios of 6.0 to 4.0 and also 1.5 to 0.5, at temperatures down to the boiling point of hydrogen, approximately 40°R. According to equation (1),

$$2H_2 + O_2 \longrightarrow 2H_2O \tag{1}$$

O/F = 8 stoichiometrically, so the above cited mixture ratios are rich in the hydrogen fuel. The classic rate studies which have been made on the combustion of hydrogen-oxygen mixtures clearly indicate that the oxidation of hydrogen occurs by a chain mechanism. The essential steps in this chain mechanism at low temperatures are listed below in equations (2-9)*. This mechanism is based upon extensive experimental and theoretical kinetic measurements and analyses made since 1928 beginning with Gibson and Hinshelwood (Ref. 1) and the experimental work of Kovalskii (Ref. 2). This mechanism has been developed upon the basis of experimental work carried out in laboratory-scale, glass-wall systems, with the intent of describing the explosive and nonexplosive combustion processes which can occur. This now classically established mechanism (Ref. 3 & 4) can yield clues as to the experimental approach which should be utilized in developing a catalytic ignition concept, useful at the extremely low temperatures of interest.

$$H_2 + O_2 \longrightarrow H + HO_2 - 55 \text{ kcal} \qquad \text{Initiation} \qquad (2)$$

$$H + O_2 \longrightarrow OH + O - 15 \text{ kcal} \qquad \text{Chain Propagation} \qquad (3)$$

$$O + H_2 \longrightarrow OH + H - 0 \text{ kcal} \qquad \text{Chain Propagation} \qquad (4)$$

$$OH + H_2 \longrightarrow H_2O + H + 14 \text{ kcal} \qquad \text{Chain Propagation} \qquad (5)$$

$$H + O_2 + M \longrightarrow HO_2 + M \qquad \text{Chain Termination} \qquad (6)$$

$$\text{and } HO_2 + \text{wall} \longrightarrow 1/2 \ H_2 + O_2$$

$$OH + \text{wall} \longrightarrow 1/2 \ H_2 + 1/2 \ O_2 \qquad \text{Chain Termination} \qquad (7)$$

$$H + \text{wall} \longrightarrow 1/2 \ H_2 \qquad \text{Chain Termination} \qquad (8)$$

$$O + \text{wall} \longrightarrow 1/2 \ O_2 \qquad \text{Chain Termination} \qquad (9)$$

In this mechanism, the basic reaction between hydrogen and oxygen gas is initiated by equation (2), which produces free atomic hydrogen and the free radical (HO_2). Once the reaction of equation (2) is thermally initiated, then the chain propagating steps of equations given by equations (3-5) propagate the chain. The chain-propagation steps are specifically represented by equations (3) and (4). In the reaction listed by equation (3) a hydrogen atom reacts with an oxygen molecule to produce two active groups, a hydroxyl radical (OH) and an oxygen atom (O). In equation (4) an oxygen atom reacts with a hydrogen molecule (H_2) to produce a hydroxyl radical (OH) and a hydrogen atom (H). In both equations (3) and (4) it is seen that one active atom (H or O)

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*A somewhat more extensive reaction scheme applies at higher temperatures, in the thermal autoignition regime of hydrogen-oxygen mixtures explored by Duff, Schott, and Kinsey, etc.

produces two active groups capable of propagating the chain; thus these reactions are basically responsible for the explosively rapid rate of the hydrogen-oxygen combustion. Equation (6) represents a chain-terminating step, as do reactions listed as equations (7-9). In each of these chain-terminating steps, a free radical (OH) or an atom (H or O) is removed from the chain-propagating steps of equations (3-5) by reacting with the wall of the container, or with an inert gas molecule (such as N_2) designated by the symbol M.

Equation (2) will not proceed of its own accord to initiate the chain process at low temperatures. One possibility would be to excite equation (2) by heating, as in the studies represented by References 1-4. The alternative approach is to essentially bypass equation (2) by otherwise providing atoms or free radicals to promote equations (3-5). Based upon well-known bond energy concepts, it is easier to prepare hydrogen atoms than oxygen atoms. With this view, the appropriate way to induce the chain process outlined by equations (3-9) is by means of chemical processes which can readily generate hydrogen atoms.

It is well established chemically that hydrogen molecules can be readily dissociated on selected catalysts into hydrogen atoms, as by equation (10).

$$H_2 \text{ (gaseous or liquid)} \longrightarrow 2H \text{ (chemisorbed on catalyst)} \tag{10}$$
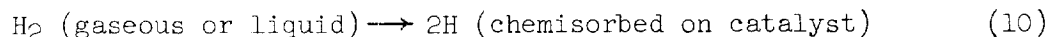
This process has been well established as occurring on the noble metal catalysts, such as platinum, palladium, and the like, and on certain other chemically prepared poly-valent metals, e.g., nickel. Therefore, these types of metal catalysts should be considered as potential ignition catalysts. The noble metal catalysts of platinum, palladium, and the like, have been prepared over the years by various chemists, with their chemical activities formulated for specific end use. It will be necessary to screen these catalysts in an experimental program to relate their ignition activities to their modes of chemical preparation. Experimental studies already started support the concept of noble metal catalyst activity. The earlier reported successful experimental ignition of gaseous hydrogen and oxygen at a temperature of approximately 160°R on a platinum catalyst substantiates the concept that chemisorbed hydrogen atoms probably can initiate the chain type of mechanisms in the gas phase which are outlined by equations (3-9).

A second means of catalyzing the ignition of hydrogen-oxygen mixtures may be considered on the basis of catalysis of the well-known ortho-para conversion of hydrogen at low temperature. It was established by Farkas and Sachsse (Ref. 5 & 6) that inhomogeneous fields generated by paramagnetic substances induce the conversion of parahydrogen to orthohydrogen as by equation (11) below.

$$p\text{-}H_2 \longrightarrow o\text{-}H_2 \tag{11}$$

Studies have indicated that the paramagnetic substances can include oxygen gas, or nitric oxide (NO) or paramagnetic ions such as copper, nickel, or the rare-earth ions. This type of catalysis involves ortho-para transition within the molecule and does not require an exchange between hydrogen atoms or the breaking of the hydrogen-hydrogen bond of the molecule (Ref. 6) as in equation (12).

$$H + p\text{-}H_2 \rightleftharpoons o\text{-}H_2 + H \tag{12}$$

It is well known chemically that certain diamagnetic compounds such as zinc oxide (ZnO) strongly adsorb hydrogen molecules at low temperatures, 160°R and below (Ref. 7). If one combines with this concept of parahydrogen conversion the presence of a stable free radical, then it is possible to obtain very rapid parahydrogen conversion at low temperatures (Ref. 8). A paramagnetic free radical, α , α diphenyl- β picrylhydrazyl,* was finely ground with zinc oxide and the conversion of parahydrogen at 85°K (153°R) was measured over this mechanical mixture (Ref. 8). The mixture of the two compounds, zinc oxide and α , α diphenyl-picrylhydrazyl, converted parahydrogen much more rapidly than either of the two compounds separately.

In this concept, the zinc oxide (ZnO) is necessary to provide strong van der Waals adsorption of the hydrogen at low temperatures, but being diamagnetic the zinc oxide does not provide a high rate of conversion of $p\text{-}H_2$ to $o\text{-}H_2$. The paramagnetic free radical α , α diphenyl- β picrylhydrazyl, probably also adsorbed on the zinc oxide, provides a free electron capable of dissociating the hydrogen. Thus a strongly promoted type of catalyst can be prepared based on equation (12), which will provide H atoms for chain initiation according to the general scheme of equations (3-9). It may also be possible to provide other known free radicals (Ref. 9) which can be evaluated. In concept, it may be possible to dissolve or suspend the free radical chemical compound in the liquid hydrogen, so that on injection of the fuel the free radicals are instantly available for H atom generation. Further analysis will be made of this concept.

2. Literature Survey

The initial emphasis of the literature study was placed on reviewing the preparation of catalytic agents which are highly specific for the chemisorption of H_2. The resulting partial dissociation of hydrogen molecules into atoms should initiate the $H_2\text{-}O_2$ combustion reaction, as discussed above. It is well known that catalysts prepared in the laboratory are more active for
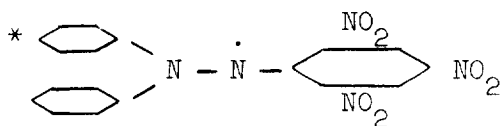
this purpose than many commercially available materials. Much information is available in the chemical literature describing very active hydrogen catalysts, available for a wide range of chemical uses. Accordingly, the literature has been studied for preparative techniques which appear feasible for the present application. Based on this survey, platinum and nickel catalysts have been prepared at The Marquardt Corporation which have produced encouraging initial performance. These have been in the form of both agglomerates and of finely divided powders. Other types of catalytic powders are to be prepared.

The following is a partial list of publications which contain pertinent information on catalytic activity of the desired type.

1. Adkins, H., and Pavlic, A.A., J.Am.Chem.Soc., 69, 3040 (1947)

2. Adkins, H., and Billica, H.R., ibid, 70, 695 (1948)

3. Brown, D.J., J.Soc.Chem.Ind., 69, 355 (1950)

4. Covert, L.W., and Adkins, H., J.Am.Chem.Soc., 54, 4116 (1932)

5. Feulgen, Ber., 54, 360 (1921)

6. Hurd, C.D., and Rudner, B., J.Am.Chem.Soc., 73, 5157 (1951)

7. Mozingo, R., ibid, 66, 1015 (1943)

8. Adams, R., et al., Organic Syntheses, Coll, Vol. 1, 463 (1941)

9. Starr, D., and Hixon, R.M., ibid, Coll, Vol. 2, 566 (1943)

10. Billica, H.R., and Adkins, H., ibid, Coll, Vol. 3, 176 (1955)

11. Neuman, F.W., et al., ibid, Coll, Vol. 3, 519 (1955)

12. Mozingo, R., ibid, Coll, Vol. 3, 685 (1955)

13. Pavlic, A.A., and Adkins, H., J.Am.Chem.Soc., 68, 1471 (1946)

14. Raney, U.S. Patent No. 1,628,190 (1927)

15. Ralls, J.W., Dodson, R.M., and Riegel, B., J.Am.Chem.Soc., 71, 3320 (1949)

16. Shriner, R.L., and Adams, R., ibid, 46, 1683 (1924)

A literature survey concerning pyrophoric metal powders has also been performed. This survey has been directed primarily towards experimental methods of preparing certain metal powders in very finely divided states. One of the more promising approaches appears to be that of utilizing electric arc dispersion techniques to produce colloidal suspensions of the metal concerned in a suitable inert liquid carrier. This is followed by controlled removal of the liquid carrier under vacuum conditions.

The following is a partial list of publications which describe both experimental techniques and theoretical considerations of interest to the proposed application of pyrophoric metal powders.

1. Bahn, G.S., Paper 64-31, 1964 Fall Meeting; Western States Section, The Combustion Institute.

2. Fatt, I., and Tashima, M., "Alkali Metal Dispersions," D. van Nostrand, Princeton, N.J. (1961)

3. Fraser, A.N., and Gibbard, J., Canad. J. Research, 10, 133 (1932)

4. Hauser, E.A., "Colloidal Phenomena," McGraw-Hill, N.Y. (1939)

5. Jirgenson, B., and Straumanis, M.E., "A Short Textbook of Colloid Chemistry," 2nd Ed., MacMillan, N.Y. (1962)

6. McBain, J.W., "Colloid Science," D.C. Heath, N.Y. (1950)

7. Mysels, K.J., "Introduction to Colloid Chemistry," Interscience, N.Y. (1959)

8. Packter, A., J. Phys. Chem., 62, 1025 (1958)

9. Richter, K., Kolloid-Z., 61, 208 (1932)

10. Shinoda, K., et al., "Colloidal Surfactants," Academic Press, N.Y. (1963)

11. Stauff, J., "Kolloidchemie," Springer Verlag, Berlin (1960)

12. Svedberg, T., "Colloid Chemistry," Chemical Catalog Co., N.Y. (1924)

13. Weiser, H.B., "A Textbook of Colloid Chemistry," 2nd Ed., Wiley & Sons, N.Y. (1949)

Phase II - Planning of Experimental Program

1. The Propellant Flow System

A liquid oxygen-liquid hydrogen propellant system has been designed for the more quantitative experimental test system to be installed in the propellants chemistry laboratory at The Marquardt Corporation. Rocket Test Laboratory on Magic Mountain (see Fig. 1). The detail design has begun, along with the selection and acquisition of line system hardware and instrumentation. Wherever possible, off-the-shelf commercial equipment with proven capability will be used to minimize cost and development time in the system. Local fabrication of system components has begun with installation at the test site planned for February.

a. Description

Further consideration of the overall experimental system has led to the selection of a pressurized gas expulsion system, rather than the positive displacement metering pump suggested in the previous report. It is believed that the pressurized gas system has the advantages of greater reliability, lower cost, and reduced lead time.

The gas expulsion propellant system operates at a supply pressure of about 200 psig. It contains four cryogenic liquid Dewars; one each for hydrogen, oxygen, and nitrogen, and a fourth for pressurized hydrogen. Gaseous helium will be used to pressurize the liquid hydrogen, and gaseous nitrogen to pressurize the liquid oxygen. The liquid volume of pressurized hydrogen will be limited to one gallon in a specially fabricated Dewar. This Dewar has a liquid nitrogen insulation reservoir, which also serves as a pre-cooling media for the gaseous helium. The other three Dewars will be provided by the commercial suppliers of the cryogenic liquids. These will be of the 100-to-200 liter size. Vacuum jacket insulation will be used on all liquid hydrogen lines and cast-in-place polyurethane foam insulation on liquid oxygen and liquid nitrogen lines. The liquid nitrogen is used to precool the liquid hydrogen line system. It will also be used for pre-run calibration of the hydrogen flow-metering instrumentation and controls system.

In both the hydrogen and oxygen systems, flow control will be accomplished by remote-control, pneumatically-operated throttling valves. Primary flow measurements will be made with venturi nozzles in the liquid phase lines upstream of the throttling valves. Secondary flow measurement will be made with cavitating venturis in the bypass flow lines, which will match the injectors in orifice size. Flow calibration of both venturis will be possible by vaporizing the liquids (or mixed-phase fluids) with a heat exchanger in the bypass lines and measuring gas flow rate through rotameters.

PROPELLANT FLOW SYSTEM SCHEMATIC

$H_2 - O_2$ POWDER METAL IGNITION STUDY

Figure 1
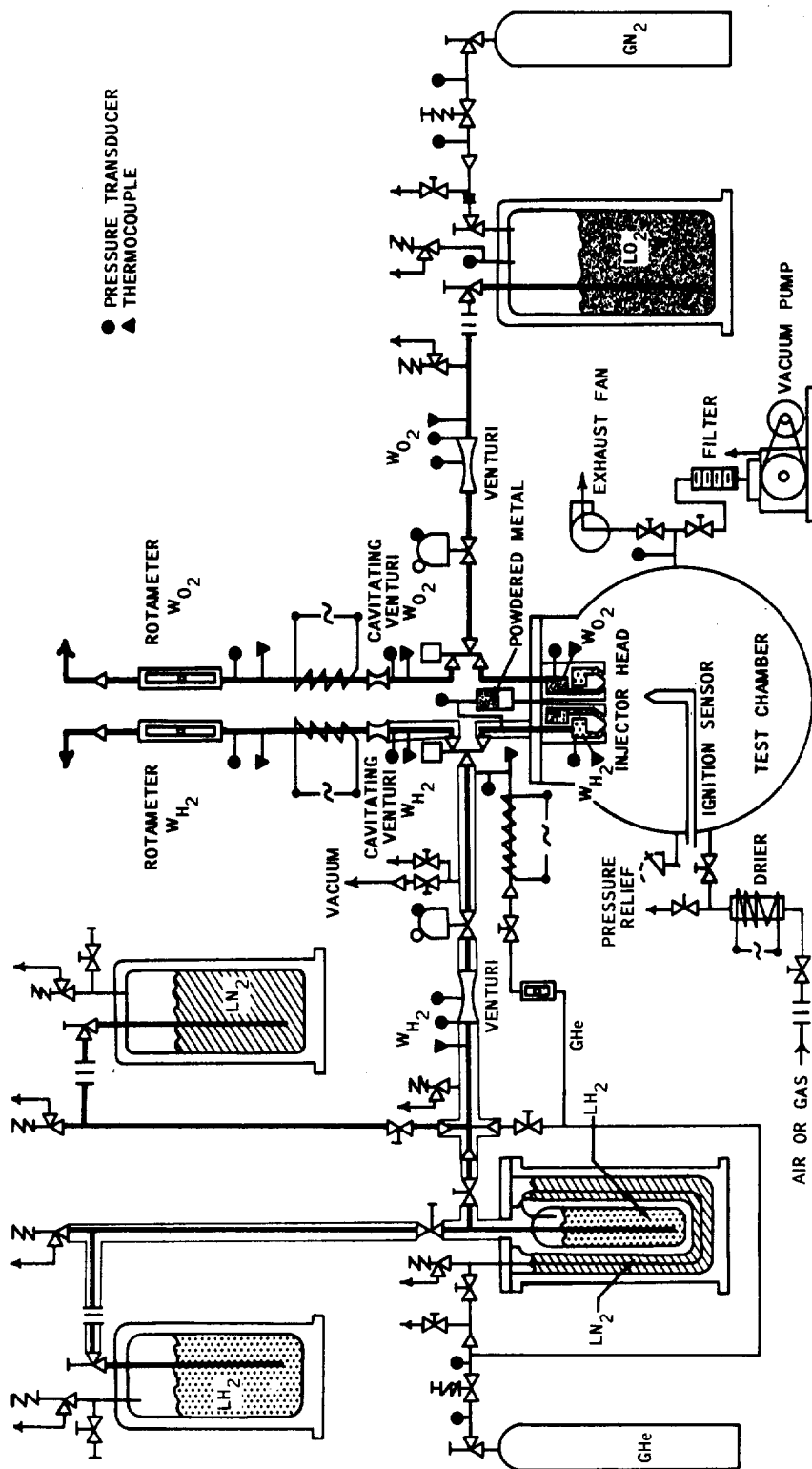
R-19,166

The diversion of flow from the bypass line to the injector head and back again will be controlled by a fast-acting, three-way solenoid valve. This valve is a balanced poppet spool type which has an equal geometry flow path in each direction. The line system pressure drop in the bypass line up to the cavitating venturi will match that of the path to the injector orifice, so that when the flow is diverted to the injector head, the preset flow rate will remain constant. Pressure and temperature instrumentation at all critical locations will verify whether this condition is met.

It is intended that the oxygen flow remain liquid and at relatively constant temperature up to the point of injection within the test chamber. The temperature of the hydrogen will be varied as part of the investigative procedure. This will be accomplished by a controlled heat leak in the jacketed section of the hydrogen line between the throttling valve and the diverter valve. Gaseous helium at a controlled temperature and flow rate will be introduced into this jacket in a manner similar to a counter-flow heat exchanger. Under these conditions, part or all of the liquid hydrogen will change phase to gas. It would then be impossible to measure flow rate at the injector orifice during mixed-phase flow. Therefore, it is important that the liquid phase be maintained in the metering venturi upstream of the throttling valve.

2. Experimental Test Chamber

a. Status

The design of the experimental test chamber has been completed and fabrication has begun. It is estimated that this item will be completed by mid-January.

b. Description

The test chamber consists of a short length of standard 18-inch-diameter pipe with two elliptical end caps. One cap is welded in place and the other connected by a hinged flange assembly to allow ready access to the interior. The injector head assembly is flange-mounted on the top center-line near the accessible end of the chamber. Two eight-inch-diameter window assemblies on either side of the injector flange allow visual coverage of the reaction zone of the injector head. A 12-inch-inside-diameter flanged-and-hinged blowoff lid assembly is also mounted on the top centerline of the chamber at the blind end. This will provide pressure relief above one atmosphere.

       The whole chamber assembly is mounted on portable stand of adjustable height. The overall dimensions are approximately four feet square by five feet high, which will allow ample installation clearance into the high hazard test cell of the propellants chemistry laboratory.

       The chamber was designed primarily as a vacuum vessel, but will withstand a 100 psig overpressure in the event of a delayed ignition and the deflagration of the propellant mixture. Connections for vacuum pump and exhaust are provided by a 2-inch-diameter pipe coupling in the blind end of the chamber. A similar connection is provided for purging air or gas near the opposite end. With these services to the test chamber, complete control over the environment can be maintained prior to an ignition attempt.

3. Flow Rates of Hydrogen and Oxygen

       The following mixture ratio (M.R.) and flow rate conditions are proposed.

M.R., O/F	Liquid O_2 Flow Rate		Liquid H_2 Flow Rate		Total Flow	
	lb/sec	lb-mol/sec	lb/sec	lb-mol/sec	lb/sec	lb-mol/sec
0.5	1.6×10^{-3}	5.0×10^{-5}	3.2×10^{-3}	1.59×10^{-3}	4.8×10^{-3}	1.64×10^{-3}
1.5	4.53×10^{-3}	1.42×10^{-4}	3.0×10^{-3}	1.5×10^{-3}	7.83×10^{-3}	1.64×10^{-3}
4.0	1.06×10^{-2}	3.31×10^{-4}	2.65×10^{-3}	1.32×10^{-3}	1.32×10^{-2}	1.64×10^{-3}
6.0	1.44×10^{-2}	4.5×10^{-4}	2.4×10^{-3}	1.19×10^{-3}	1.68×10^{-2}	1.64×10^{-3}

Total flow rates were determined by fixing the total molar flow rate to be constant. This was done in order to make a more uniform load on the environmental chamber vacuum system. The latter sees, in effect, the number of moles of gas to be evacuated, rather than the number of pounds.

       The above flow rates are target values, and may be modified as necessary. In particular, the maximum and minimum values for the oxygen flow rate may have to be altered slightly due to venturi pressure drop considerations.

Phase III - Experimental Study

1. Preliminary H_2-O_2 Ignition Studies

Concurrent with the design of the more quantitative main test apparatus described above, supplementary experimental ignition work has been conducted in the Physical Chemistry Laboratory. These tests have utilized gaseous H_2 and O_2 at ambient pressure, in the temperature range from ambient to near the boiling point of liquid O_2. The primary purpose of this work is to provide preliminary catalyst evaluation. Testing to date has utilized a platinum catalyst prepared by a method similar to that described in Reference 10. The information obtained is to be used to support and expedite the testing program to be performed subsequently with the main experimental ignition apparatus now being assembled.
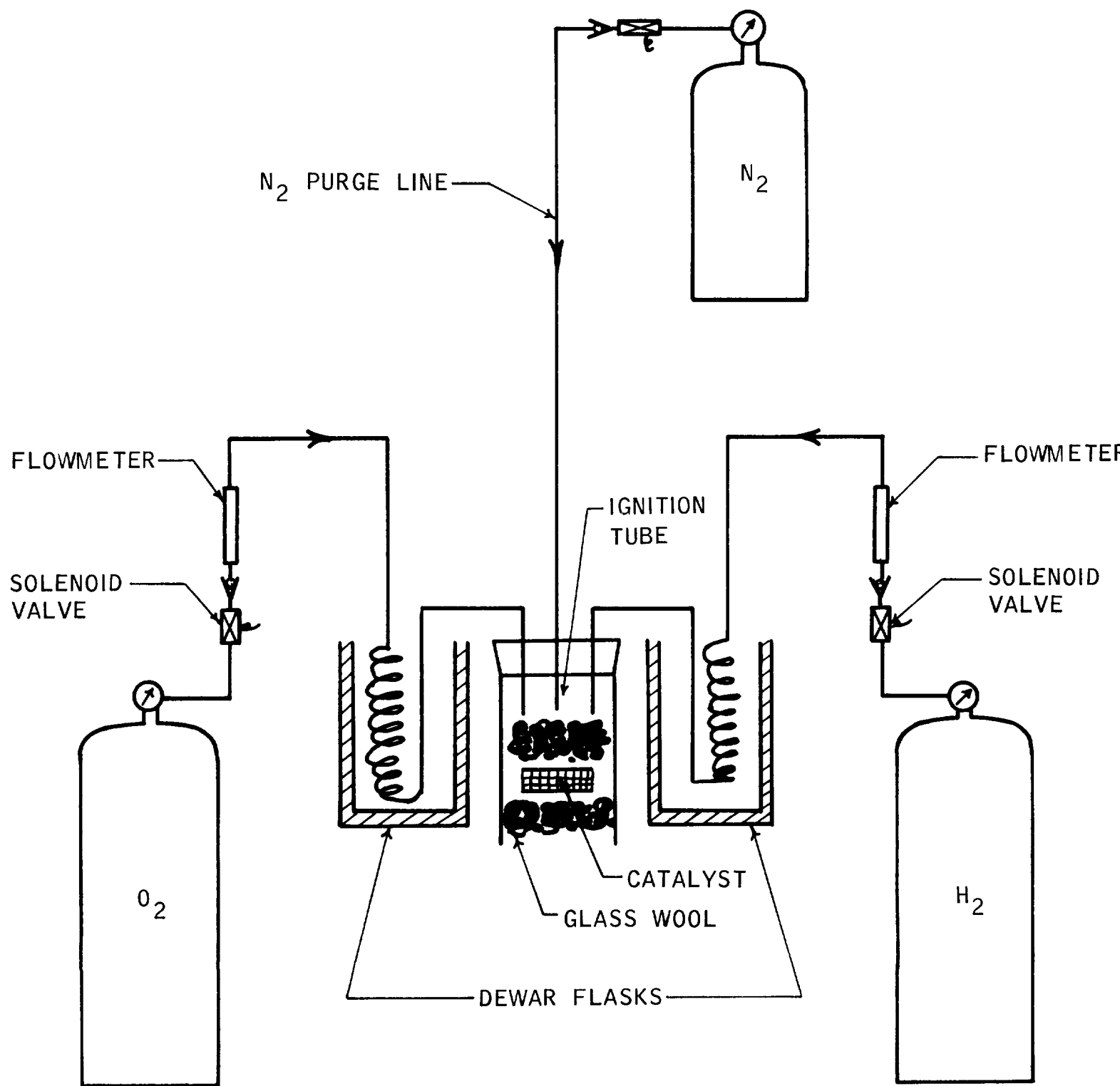
2. Apparatus

The first tests were performed in the Mark I igniter, shown schematically in Figure 2. The catalyst, contained on either glass wool or a 200-mesh nickel screen, is mounted in a small glass tube, positioned behind a safety-glass shield. The H_2 and O_2 control valves (located at the flowmeter inlets) are adjusted to provide the desired flow rates whenever the H_2 and O_2 solenoid valves are activated. Each gas is passed through a copper coil into a Dewar flask, in which liquid N_2 or another cooling medium may be placed. The insulation around the top of the ignition tube provides a reservoir for liquid N_2, to obtain more effective chilling of the inlet gases and the ignition tube. Copper/constantan thermocouples are installed in the O_2 and H_2 lines just upstream of the ignition tube inlet.

Glass wool is used to mix the gas streams before contact with the catalyst. The other end of the ignition tube is plugged with glass wool. The flow rates of O_2 and H_2 are set at low values so that the ignition is not violent. A purge of N_2 is used before and after each ignition test.

Initial tests with this apparatus used visual detection of ignition. Later, a platinum/platinum-rhodium thermocouple (0.005 in. dia.) was also used for this purpose. The output of the latter, suitably amplified, was displayed on a Hewlett-Packard Model 130A oscilloscope. Using small amounts of the newly prepared platinum-powder catalysts, ignition has been demonstrated with both H_2 and O_2 gases cooled to near liquid N_2 temperature. The ignition tube plus catalyst was also chilled substantially by the liquid N_2 in these tests. Reignition was repeatedly obtained under these conditions.

PRELIMINARY H_2-O_2 IGNITION ASSEMBLY
MARK I

N_2 PURGE LINE

N_2

FLOWMETER

IGNITION TUBE

FLOWMETER

SOLENOID VALVE

SOLENOID VALVE

O_2

CATALYST
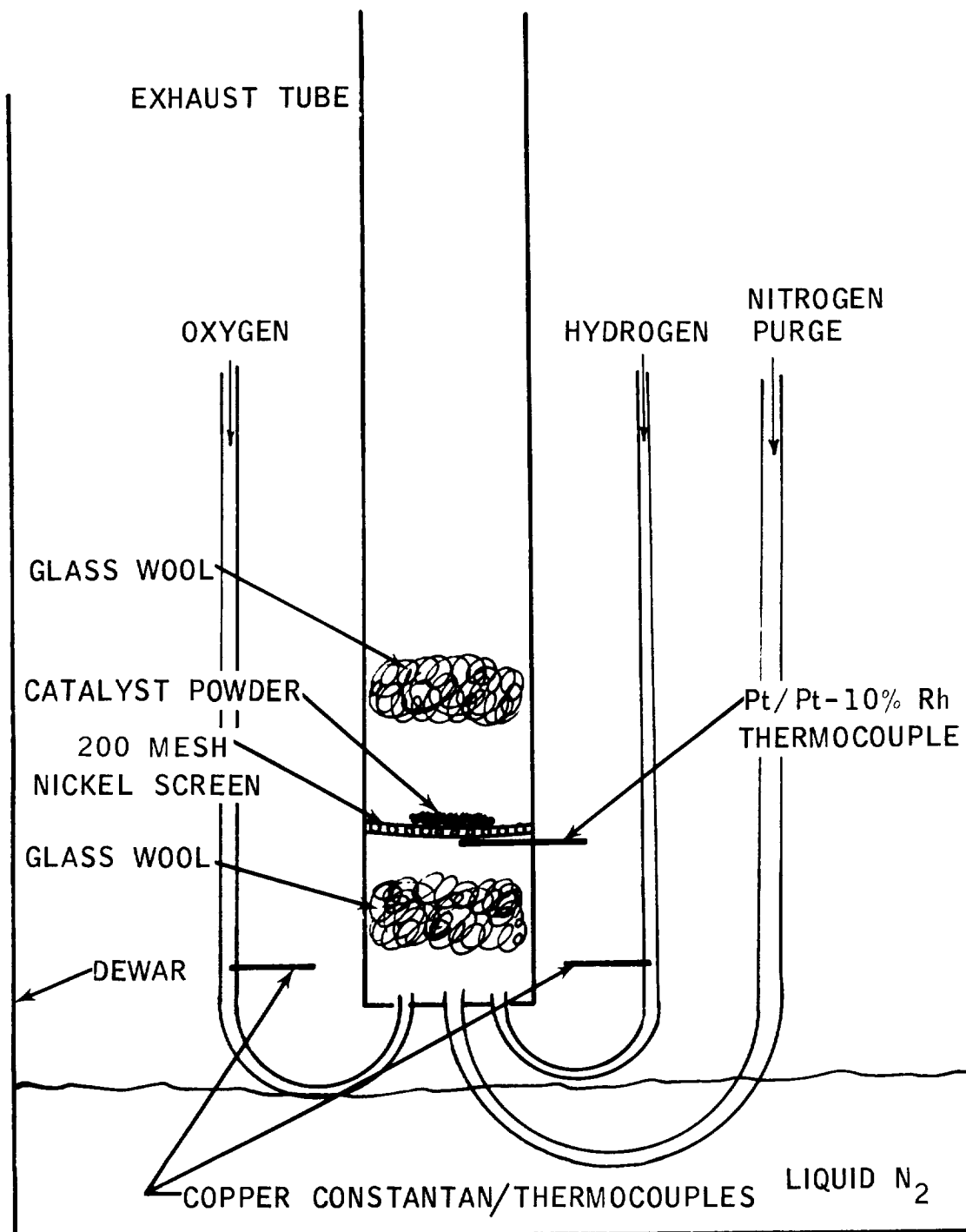
GLASS WOOL

H_2

DEWAR FLASKS

Figure 2

The catalyst used in these tests was utilized for 6 days with no noticeable qualitative deterioration of ignition characteristics. It was left in position in the ignition tube during this time, under an atmosphere of N_2 when not in use.

The next experimental set-up, the Mark II igniter, permitted insertion of the entire assembly, including catalyst and gas inlet lines, into a liquid N_2 Dewar. This permitted more uniform control for low temperature tests. This apparatus is shown in Figures 3 and 4. With the fast response thermocouple in the position shown in Figure 3, the oscilloscope trace indicated the initial temperature rise of the catalyst bed caused by the water formation reaction. Using this more rugged apparatus, higher gas flow rates (with more vigorous ignitions) could be tested.
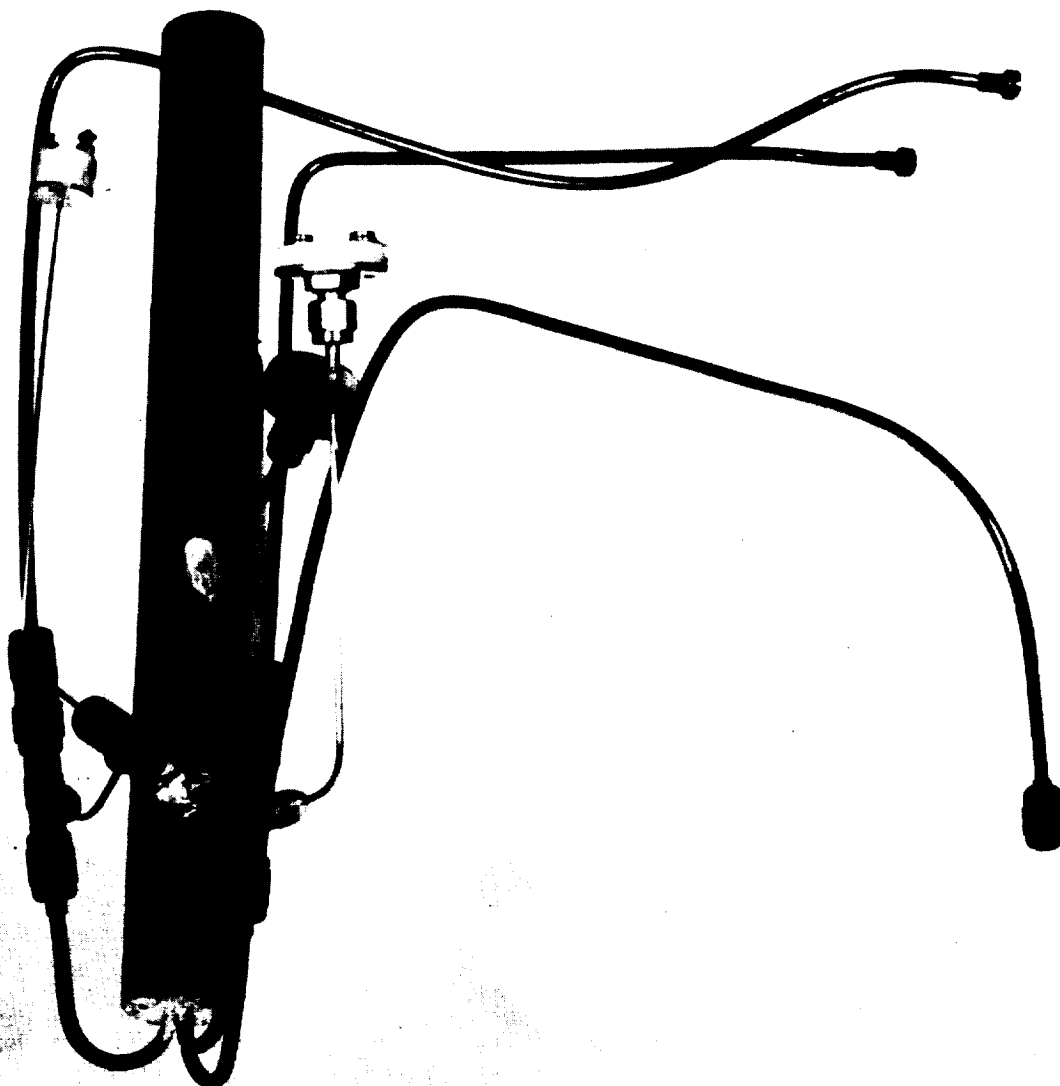
Due to the relatively large void area directly below the catalyst, this device could not be operated with the large copper exhaust tube immersed in liquid N_2. Under these conditions, the incoming gaseous O_2 would liquefy, and there would be no net flow of gaseous O_2 past the catalyst. It was not feasible, due to safety considerations, to attempt repeated ignitions with liquid oxygen in the Physical Chemistry Laboratory. Ignitions were usually obtained, however, when the liquid N_2 covered the U bend of each of the gas inlet tubes.

Using this apparatus, an ignition was obtained with both gases and the catalyst near the temperature of boiling liquid O_2 (162°R at 760 mm) by the following procedure: With all three gases flowing, liquid N_2 was added to the Dewar until the copper exhaust tube was immersed above the level containing the catalyst. The N_2 flow rate was so much larger than the O_2 and H_2 flows (which were stoichiometric) that no ignition occurred. After the system had chilled down thoroughly, the H_2 flow was shutoff, and the O_2 flow left on at a very low value. This step insured that no heat was imparted to the system by small amounts of water formation on the catalyst. The system was left at these conditions for about one hour, during which time the liquid N_2 level in the Dewar had been slowly dropping. During this period there was no net flow of gaseous O_2 out of the exhaust tube, due to condensation. As the liquid N_2 level dropped to where it was just touching the U bend of the O_2 inlet tube, gaseous flow of O_2 out of the exhaust tube was observed. This implied that the temperature of the catalyst was very near that of the liquid O_2 boiling point, since a pool of liquid O_2 had been collecting in the lower part of the exhaust tube. As soon as O_2 output flow was observed, the N_2 purge flow was shutoff, and H_2 and O_2 were admitted simultaneously. After a delay of several seconds, a powerful ignition occurred.

IGNITION DEVICE MARK II

EXHAUST TUBE

OXYGEN HYDROGEN NITROGEN PURGE

GLASS WOOL

CATALYST POWDER

200 MESH NICKEL SCREEN

GLASS WOOL

Pt/Pt-10% Rh THERMOCOUPLE

DEWAR

COPPER CONSTANTAN/THERMOCOUPLES LIQUID N_2

R-19,174

Figure 3

IGNITION DEVICE MARK II

Figure 4

Although qualitative, these results indicate that this catalyst material is capable of producing ignition when the catalyst, the hardware, and both gases are near the temperature of the liquid O_2 boiling point (162°R). At least part of the long delay time for the ignition is accounted for by the fact that the linear velocity of the gases in the exhaust tube below the catalyst was very low at the time of ignition.

The next apparatus, the Mark III igniter, provided more positive control and measurement of the temperature of the gases and of the catalyst. This device is shown in Figures 5 and 6. It also reduced the time lag involved from activation of the solenoid valves to the establishment of steady flow of both gases past the catalyst zone. This was accomplished by utilizing small diameter conduits for all gases, up to the sudden enlargement at the catalyst zone.

The main body of this device is brass. The lower body portion is a tube with three slots cut through the wall. The thin body wall and the slots reduce the thermal path, allowing a measure of temperature control of the gases and catalyst by varying the immersion depth of the apparatus in liquid nitrogen.

The O_2 and H_2 enter the unit from opposite sides into a central port, which leads to the catalyst zone. A copper/constantan thermocouple placed in the central port measures gas temperature. The nitrogen flows in through a side port, purging the reaction zone.
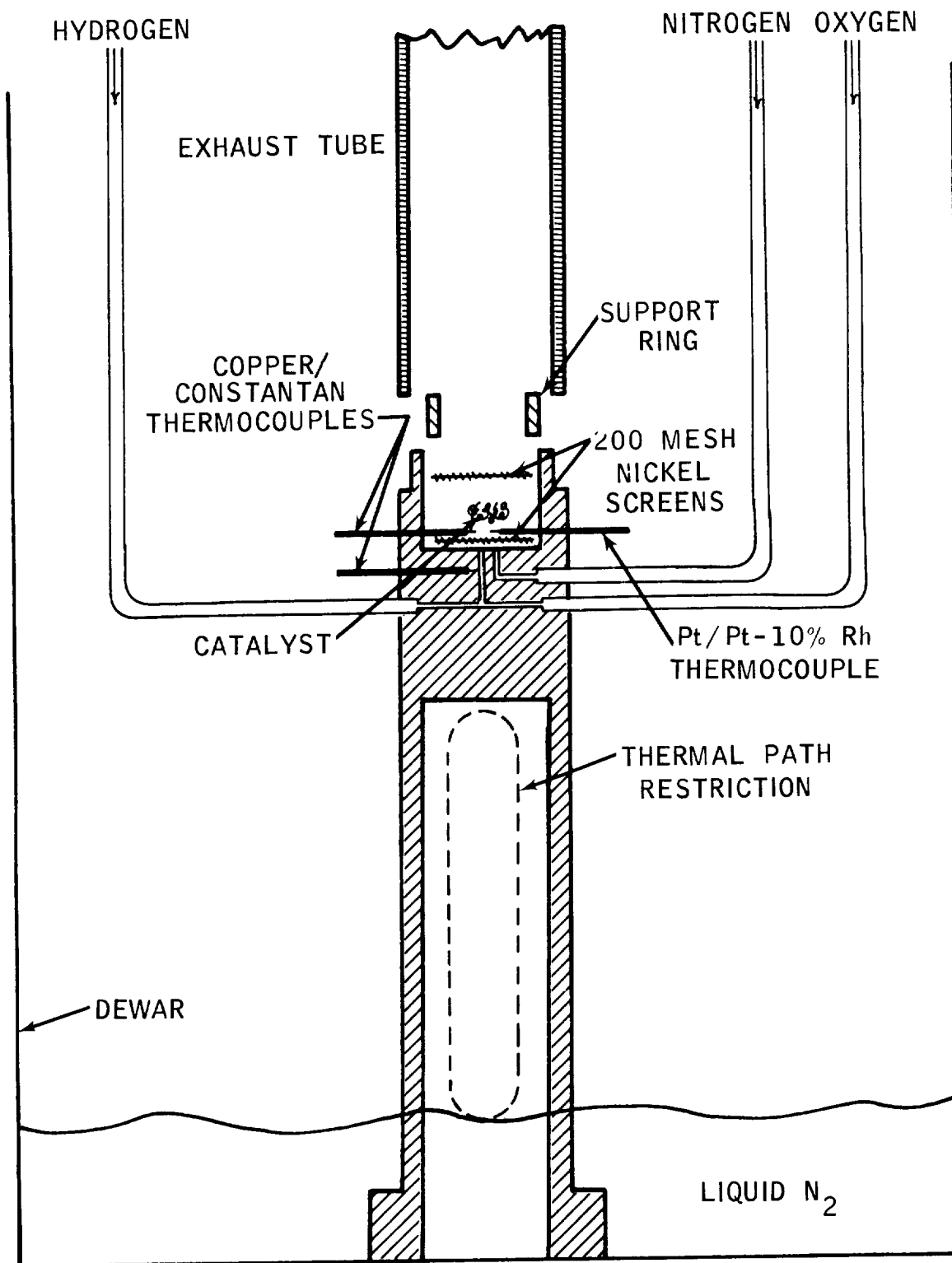
Both ports open into a sudden enlargement, which contains the catalyst and two thermocouples, all of which are held in place between two sections of 200 mesh nickel screen. One thermocouple is copper/constantan, to measure the catalyst temperature. The second is a fast response Pt/Pt-10% Rh thermocouple (0.005 in. dia.) to measure the response time of the reaction.

The position of the catalyst is maintained by a support ring which is placed over the top section of nickel screen. The copper exhaust tube is positioned by slipping onto the brass base unit.
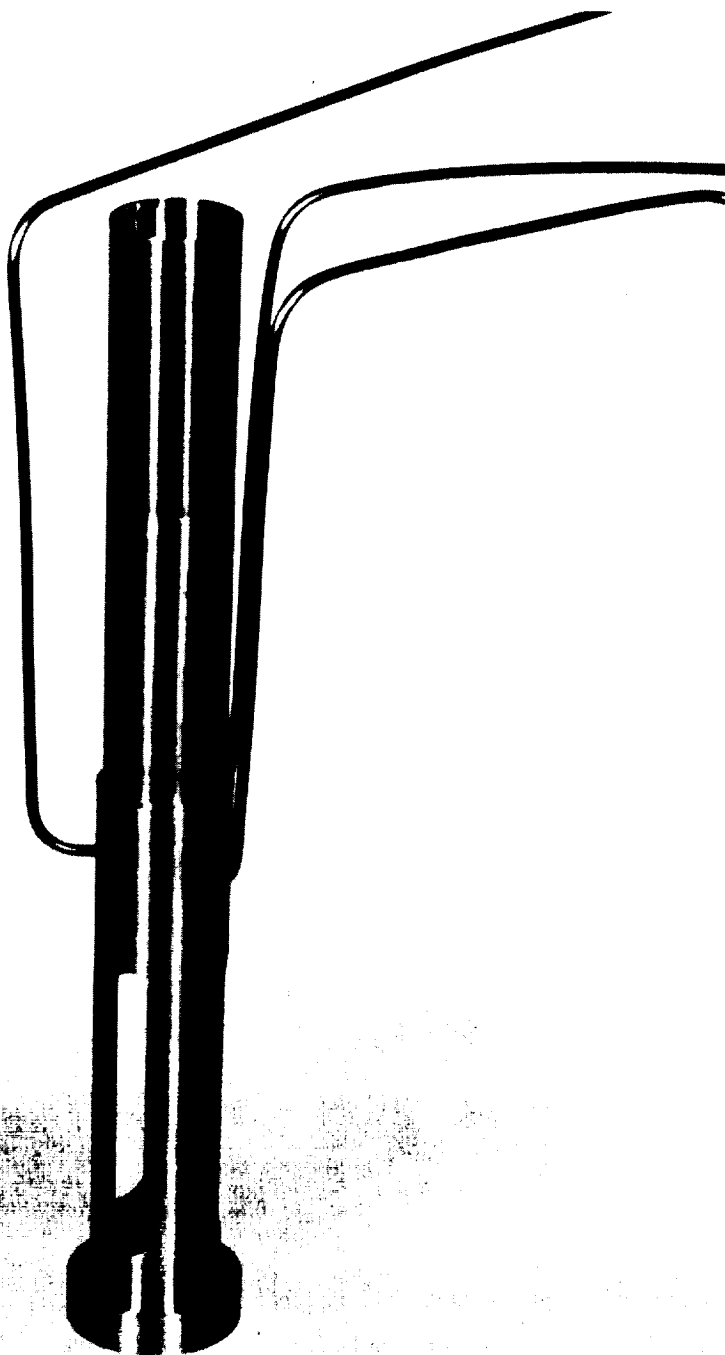
3. Preliminary Ignitions

A photograph of this device in operation is shown in Figure 7. The outputs of the two copper/constantan thermocouples are measured by two Leeds and Northrop millivolt potentiometers. Due to the small diameter gas conduits used, the temperatures of the H_2 and O_2 gas streams are quite sensitive to the temperature of the surrounding metal. The output of the Pt/Pt-10% Rh thermocouple is amplified by a Kintel Model 111BF voltage amplifier, and portrayed on a Tektronix Type 564 storage oscilloscope. Photographs of the latter are made with a Tektronix C-12 oscilloscope camera.
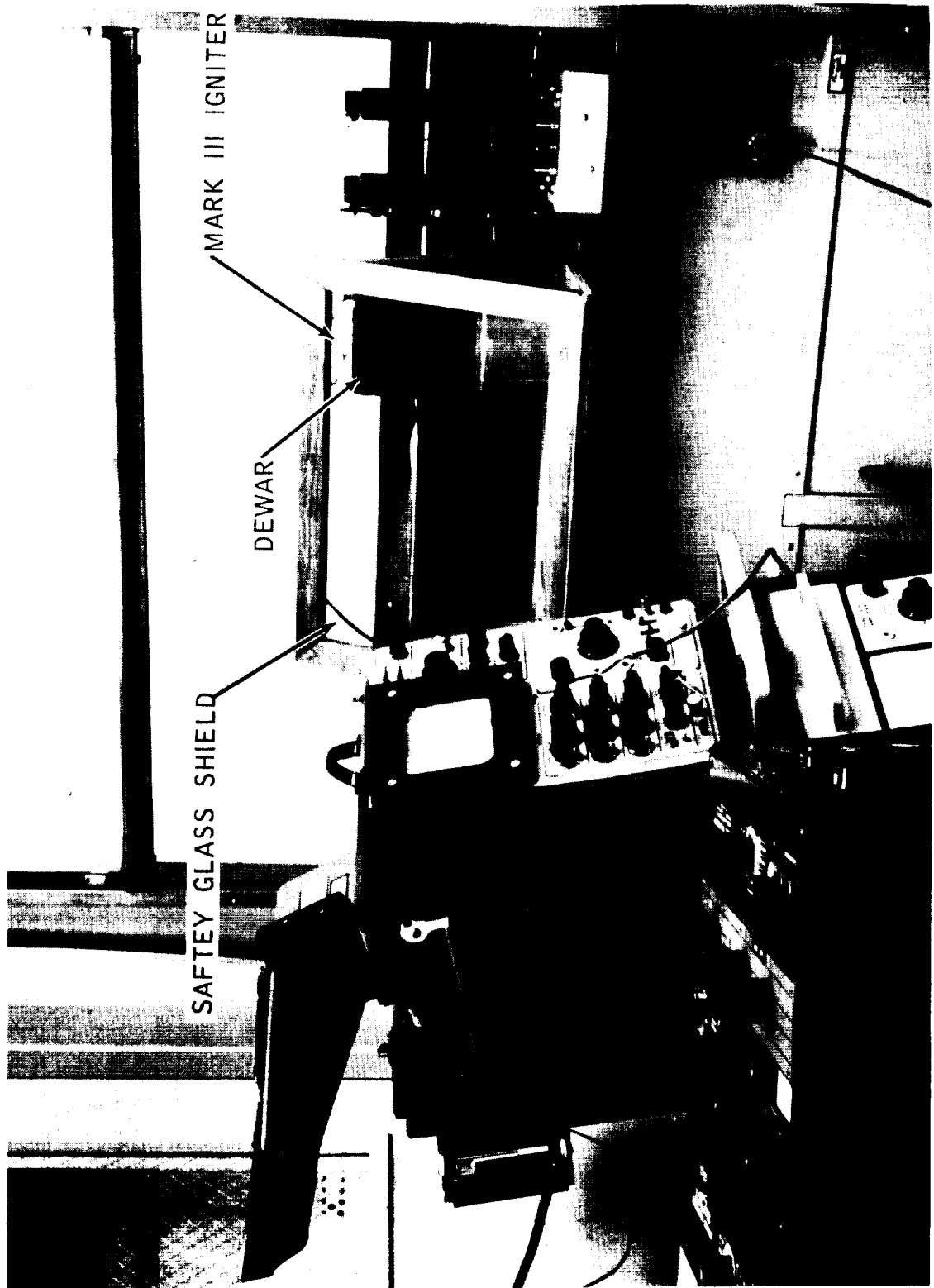
IGNITION DEVICE   MARK III

HYDROGEN

NITROGEN OXYGEN

EXHAUST TUBE

SUPPORT RING

COPPER/ CONSTANTAN THERMOCOUPLES

200 MESH NICKEL SCREENS

CATALYST

Pt/Pt-10% Rh THERMOCOUPLE

THERMAL PATH RESTRICTION

DEWAR

LIQUID N_2

INGITION DEVICE   MARK III

EXPERIMENTAL IGNITION ASSEMBLY
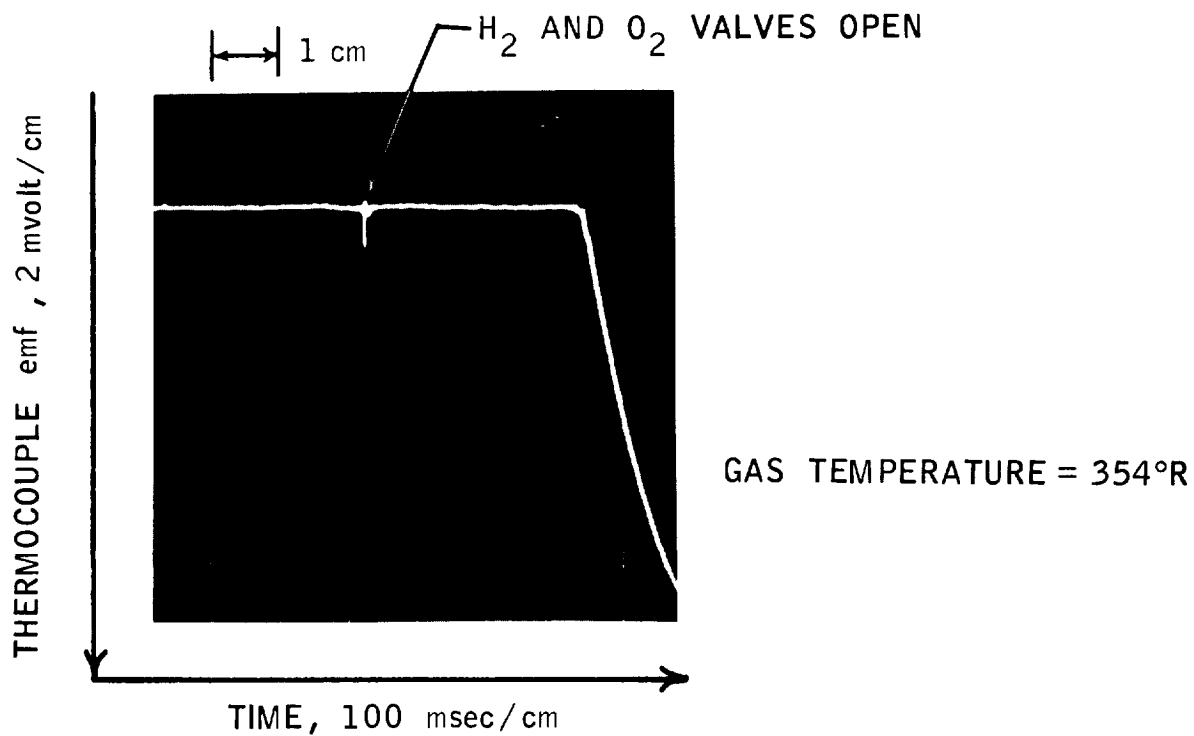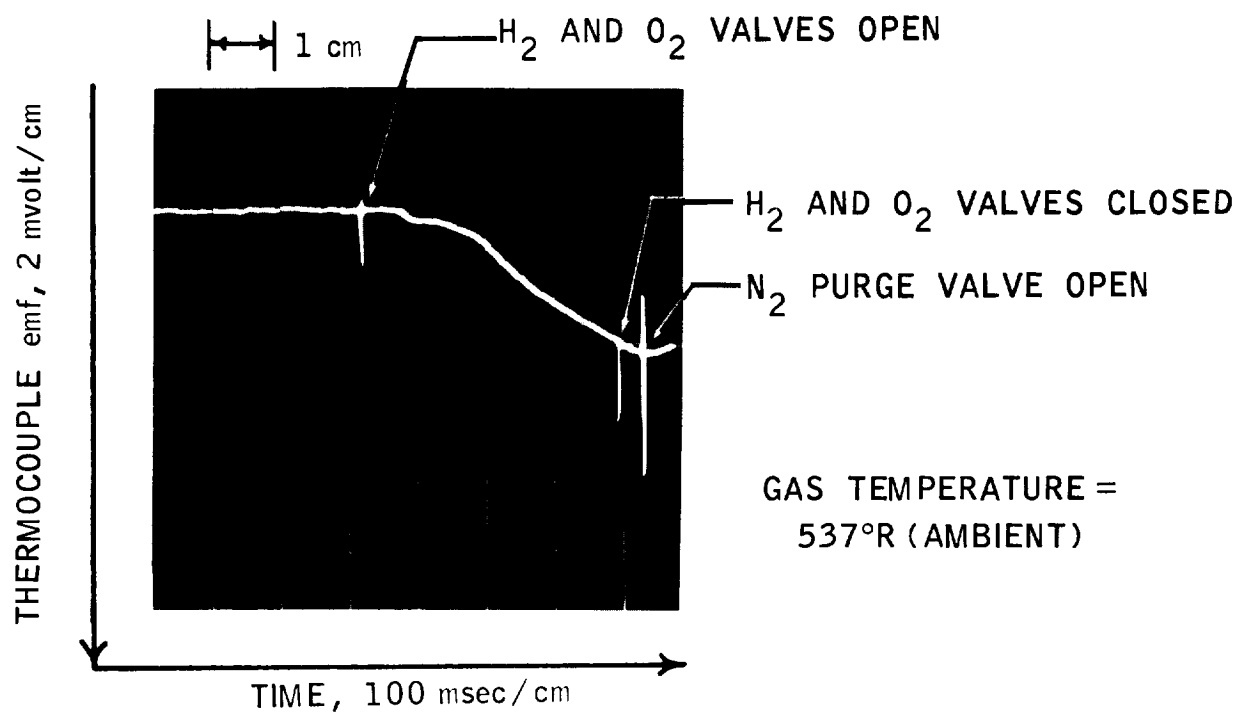
MARK III IGNITER

DEWAR

SAFTEY GLASS SHIELD

When operating at low temperatures, gas temperatures are measured by flowing only H_2 (or O_2) at one time. This is necessary to avoid heating of the catalyst bed, since there is some reaction at the catalyst with the Mark III igniter even when the N_2 purge is flowing. During low temperature runs, the reading of the top copper/constantan thermocouple (placed near the catalyst) is normally about 10-15°F higher than that of the gas temperature thermocouple.

Some of the results obtained with this device are shown in Figure 8, which are photographs of the oscilloscope trace of the fast response Pt/Pt-10% Rh thermocouple. The top trace was taken at room temperature. The reaction time is measured from the first pip, which is the opening of the O_2 and H_2 solenoid valves. It can be seen from this figure that the thermocouple began to show an increased temperature (due to water formation on the catalyst) after about 80 millisec. The small-scale detonation accompanying ignition had occurred before the second pip, which was caused by closure of the O_2 and H_2 valves. The third, larger pip, was due to opening of the N_2 purge solenoid valve. In general, there is no pip on the thermocouple trace due to the detonation itself, since the latter presumably occurs slightly downstream of the catalyst section. The thermocouple trace normally continues at a decreased temperature level following the ignition.

The lower photograph in Figure 7 was obtained at a gas temperature of 354°R (197°K). It can be seen that there was an apparent delay of about 300 millisec after valve activation, followed by a rapid ignition process. There have not yet been sufficient data taken to indicate whether or not an ignition delay of this magnitude is characteristic of this catalyst. Further tests to obtain ignition with this particular catalyst specimen at gas temperatures near the liquid O_2 temperature were unsuccessful.

In this respect it should be noted that the above series of tests, which were conducted at the end of the report period, utilized catalyst specimens which had been prepared six weeks previously. The catalyst had been stored under vacuum in the interim, but the storage vessel had been opened (after admitting argon) on numerous occasions to withdraw samples. The possibility of a gradual loss in catalyst activity must therefore be considered, particularly when it is recalled that earlier samples of this batch of catalyst had been used in successful ignitions at temperatures near 162°R (90°K). It is of interest to note that, earlier in the report period, a specific catalyst specimen was utilized for eight days, and was still producing ignitions at the end of this time when it was removed. During this period the specimen was left in place in the ignition vessel (Mark II). Further work concerning catalyst activity and durability will be performed in the next report period, utilizing the Mark III igniter.

OSCILLOSCOPE INGITION TRACES

|← 1 cm →| ⎯ H$_2$ AND O$_2$ VALVES OPEN

THERMOCOUPLE emf, 2 mvolt/cm

⎯ H$_2$ AND O$_2$ VALVES CLOSED

⎯ N$_2$ PURGE VALVE OPEN

GAS TEMPERATURE =
537°R (AMBIENT)

TIME, 100 msec/cm

|← 1 cm →| ⎯ H$_2$ AND O$_2$ VALVES OPEN

THERMOCOUPLE emf, 2 mvolt/cm

GAS TEMPERATURE = 354°R

TIME, 100 msec/cm

4. Other Catalysts and Pyrophoric Metal Powders

A sample of Raney nickel was prepared by a procedure similar to that described in Reference 11. The term "Raney nickel" refers to a class of nickel catalysts obtained by leaching out the aluminum from a nickel-aluminum alloy. Raney nickels are of interest to the present program since they are strongly pyrophoric and are excellent catalysts for H_2 chemisorption. They thus have the capability of producing ignitions by two different mechanisms. One is the formation of hydrogen atoms as a result of H_2 chemisorption, with resulting ignition due to the reaction of the hydrogen atoms with oxygen molecules. This is the mechanism believed responsible for the ignitions presently being obtained with the platinum catalyst. The second mechanism is the direct, pyrophoric reaction of the nickel powders with O_2, with the resulting heat liberation initiating the H_2-O_2 reaction chain.

Testing of these nickel powders to date has consisted of qualitative observations of their pyrophoric nature at ambient conditions, as a function of various methods of preparation and pretreatment. It has been demonstrated that, as expected, the Raney nickel powders are very pyrophoric at room temperature, and this characteristic is apparently strongly increased by a vacuum pretreatment. Further evaluations, including preliminary quantitative ignition tests, are to be performed shortly.

Alternative methods of preparing other catalytic and pyrophoric metal powders have been evaluated and the necessary equipment for their preparation is being assembled. In particular, it appears to be desirable to prepare very finely divided pyrophoric metal powders by forming colloidal suspensions of the metal concerned in a suitable liquid carrier, followed by careful removal of the carrier under vacuum conditions.

MONTHLY STATUS

Overall Progress - Current
Problems Impeding Progress - None
Corrective Action - None
Work to be Performed during next Report Period -

Phase I - Analytical Studies

1. Literature Review - The basic literature review on the preparation of active noble metal catalysts and on preparation of pyrophoric metal additives has been completed. A small amount of additional review will be required during the experimental program.

2. Analysis of Experimental Models - A theoretically reasonable model of the activation process and the catalytic requirements for this model has been completed and is reviewed in this report. There will be a continuing reevaluation of this portion of the program during the study.

Phase II - Planning of Experimental Program - The major engineering design and analysis has been completed for the fabrication of an experimental ignition apparatus capable of giving quantitative results. Procurement and construction of the apparatus is being initiated in the next contract month. It is expected that the apparatus will be assembled and functioning by the next quarterly report date.

Phase III - Experimental Study - Initiated. Further ignition tests with better quantitative temperature, flow, and timing controls have been performed in the improved interim laboratory scale apparatus, using gaseous hydrogen and gaseous oxygen. These screening tests will be continued while the major apparatus discussed under Phase II above is being completed.

Phase IV - Evaluation of Experimental Data - Initiated. Preliminary experimental data generated in Phase III above are being evaluated.

QUARTERLY EXPENDITURES FROM SEPT. 15 TO DEC. 18, 1964

Total Man-hours - 1226 (Equivalent to 21% of planned hours)

Estimated Total Costs - $24,596 (Equivalent to 23% of planned dollars)

Estimated Commitments - $ 264 (Purchase of the raw materials and components
for the basic experimental apparatus, as now
designed, has just begun)

REFERENCES

1. Gibson and Hinshelwood, Proc. Roy. Soc., 118A: 170 (1928); 119A: 591 (1928).

2. A.A. Kovalskii, Phys. Z. Sowjet. 4, 723 (1933).

3. Semenov, N.N., Some Problems of Chemical Kinetics and Reactivity, Vol. 2, p. 47, Pergammon Press, New York (1959).

4. Lewis, B. and G. Von Elbe, Combustion, Flames and Explosions of Gases, Academic Press, New York (1961).

5. Farkas, L. and H. Sachsse, Sitzber. preuss. Akad. Wiss. 1933, 268

6. Farkas, L. and H. Sachsse, Z. Physik. Chem., B23, 1, 19 (1933).

7. Taylor, H.S. and H. Diamond, J. Am. Chem. Soc., 55, 2613 (1933).

8. Turkevich, J. and P.W. Selwood, J. Am. Chem. Soc., 63, 1077 (1941).

9. Ingram, D.J.E., Free Radicals, Butterworth Scientific Publications, p. 136, London (1958).

10. Feulgen, Chem. Ber., 54, 360 (1921).

11. Pavlic, A.A. and Adkins, H., J. Am. Chem. Soc., 68, 1471 (1946).

ESTIMATED PROGRESS SCHEDULE

NATIONAL AERONAUTICS & SPACE ADMINISTRATION CONTRACT No. NAS8-11250

The Marquardt Corporation Contract No. 358 - September 16, 1964

For: Feasibility Study of Oxygen/Hydrogen Powdered Metal Ignition

	MONTHS FROM GO-AHEAD	FUND ESTIMATE	TIME Man Hours
PHASE I - ANALYTICAL STUDIES		$ 9,744	
1. Literature Review			320
2. Analysis of Experimental Models			160
PHASE II - PLANNING OF EXPERIMENTAL PROGRAM		$ 9,593	500
PHASE III - EXPERIMENTAL STUDY		$ 79,806	640
1. Catalyst Preparation			
2. Hypergolic Ignition Measurements			3,620
PHASE IV - EVALUATION OF EXPERIMENTAL DATA		$ 9,712	500
REPORTS			
Monthly Status Reports			
Quarterly Reports			
Final Report			
		$108,855	5,740

(Months columns numbered 1 through 12)